PROCESS FOR PREPARING METAL SOAP MIXTURES

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10 Claims

ABSTRACT OF THE DISCLOSURE

Mixtures of a metal soap (I) melting below 40° C. and of a metal salt (II) not melting below 140° C., are formed by reacting a saturated, straight chain Cn-Cm fatty acid with a suitable metal compound of metal (II) at a temperature above 100° C. in a melt of metal soap (I), or in an excess of the fatty acid. Organic additives melting below 140° C. may be present.

This invention relates to a process for preparing a mixture of metal soaps. Metal salts of long-chain fatty acids, also known as metal soaps, may be prepared either by a precipitation method carried out in an aqueous medium or by a fusion process in anhydrous media. Whereas almost all metal soaps can be prepared by the precipitation method, only a limited number of them can be produced by the fusion process.

In the fusion process, metal oxides, hydrates and metal salts of volatile acids, such as formates, acetates or carbonates, are reacted in the melt with the corresponding fatty acids. The required temperatures are normally in the range of from 120° C. to 140° C., by reason of the relatively low reactivity of some of the reactants and of the displacement of reaction equilibrium towards formation of a metal soap by elimination of the water of reaction or of the volatile acid which acts as metal carrier. The applicability of the fusion process is determined by two conditions, namely:

(1) Both the fatty acid employed and the metal soap formed must be stable at the reaction temperature, and the metal soap in particular must not undergo discoloration or tend to resinify.

(2) At the reaction temperature, the melt must be of such thin-flowing consistency as to render a correct mixing of the reactants possible.

Although the condition of thermal stability at 120° C. to 140° C. is satisfied by most of the fatty acids and metal soaps, many of the latter do not melt in this temperature range or, if they do, cannot form a thin-flowing melt. For example, among the metal soaps of stearic acid, only lead, zinc, magnesium and cadmium stearates display a sharply defined melting point and yield thin-flowing melts; others, like dibasic lead stearate and lithium stearate, do not melt at all, or do not have a sharply-defined melting point but transform into a plastic state with several transition temperatures, as in the case of calcium, barium, strontium and aluminium stearates.

The first-mentioned, low-melting group of metal soaps are referred to hereinafter as Type I soaps, while the soaps having high melting temperatures are designated as Type II soaps. The metal soaps belonging to the high-melting or plastifying group II could be prepared hitherto only by the precipitation method which, while yielding purer and more voluminous products than the fusion method, is substantially more complicated and expensive, the production costs being further increased by the more complicated equipment and the additional drying process involved. In addition, there are a number of applications which do not require small particle sizes, for example the stabilization of polyvinylchloride.

Metal soaps prepared by the fusion method, e.g. lead stearate, have already been used for stabilizing polyvinylchloride. In order to achieve a synergistic stabilizing effect, combinations of metal soaps of different metals, e.g. the known systems made up of barium-cadmium laurate, lead-calcium stearate and zinc-barium laurate, are employed.

A method of preparing metal soap combinations which has now been found, making possible the preparation of metal soap combinations consisting of a metal soap of Type I yielding a thin-flowing and thermally stable melt, and of a plastic or non-melting metal soap of Type II by a very simple fusion process.

According to the present invention, there is provided a process for preparing a mixture of metal soaps comprising from 10 to 40% by weight of at least one metal soap melting below 140° C. and yielding a thin-flowing melt (Type I), and 60 to 70% by weight of at least one metal soap which does not melt or melts only above 140° C. (Type II). In this process, a metal soap of Type II is prepared by reacting a saturated, straight-chain fatty acid having 8 to 24 C-atoms with a metal oxide or a metal salt of a volatile acid at a temperature above about 100° C. in a melt of a Type I metal soap, or in an excess of the fatty acid the excess of which is then converted into the Type I metal soap.

Optionally, one or more organic components which have a melting point below 140° C., which are compatible with the soaps and which do not react with the reactants, can be present in the mixture.

The Type II metal soap is thus prepared in a liquid medium, which need not be eliminated after the reaction, because it is a component of the desired metal soap mixture, and which may contain up to about 20% by weight of one or more organic compounds melting below 140° C.

This molten medium comprises either the melt of the first-obtained metal soap of Type I or of a molten fatty acid, which is employed in such a quantity that its excess after preparation of the Type II metal soap will suffice for conversion to Type I metal soap. In the final phase there are obtained either dispersions of Type II metal soaps in the melt of Type I metal soaps or eutectic melts of the two metal soap types, or a solution of the Type II metal soap in the melt of the Type I metal soap with a viscosity sufficiently low to allow intimate mixing.

The metal soap mixtures prepared by the present process contains as its Type I metal soap preferably one or more of the soaps of a straight-chain fatty acid having from about 8 to about 24 C-atoms and of zinc, cadmium or magnesium, and the normal lead soap of these fatty acids. The preferred Type II metal soaps are those formed by the metals lithium, potassium, sodium, barium, calcium, strontium and aluminium with straight-chain fatty acids having from about 8 to about 24 C-atoms, as well as basic lead salts, such as mono- and di-basic lead soaps of these fatty acids.

In order to facilitate the reaction or to lower the viscosity, it is advisable in some cases to employ organic additives melting at about 25° C., which do not hinder the intended application of the metal soaps and which are not incompatible therewith. Where the metal soap mixtures are intended for use as stabilizers for polyvinylchloride, the organic components used may be lubricants or plasticizers of the most varied kind. The conditions determining their applicability are that they must be capable of forming melts in the temperature range of from about 25° C. to about 140 C., and, where the metal component is constituted by a metal oxide or hydroxide should not react with the metal component. The organic component melting in the range of from about 250 C.
component melting in the range of from about 25°C to about 140°C is in most cases employed in an amount varying between 0 and about 20% by weight of the total mixture. However, in certain cases it may be advantageous to employ larger amounts of one or more organic additives, for example, where the metal soap is to be used as a stabilizer for polyvinylchloride and the organic component is a compound which is to be incorporated as plasticizer into the plastic in large amounts.

The organic component can be a phthalic acid ester, such as diphenyl phthalate, dibenzyl phthalate or diethylhexyl phthalate; a hydrocarbon, such as a natural paraffin, a synthetic paraffin or a polyethylene-wax; a fatty alcohol, such as palmityl alcohol, stearyl alcohol; a wax ester, such as cetyl palmitate, myristyl palmitate or stearyl stearate; a natural wax such as carnauba wax; a triglyceride, such as glycerol tri-12-oxystearate, glycerol tri-palmitate, glycerol tristearate; or a fatty acid amide such as stearic amide and ethylenediamine diesterate.

The lowermost limit of the quantity of organic component is determined by the viscosity of the mixture of Type I and Type II metal soaps obtained. The quantity of organic component must be such, that the reaction mixture is sufficiently viscous to ensure a thorough mixing.

The ratio of Type I and Type II metal soaps will be selected in accordance with the intended application and the viscosity at the reaction temperature. The viscosity of the melt increases proportionally to the content of Type II metal soaps, so that the limit of sufficient miscibility is soon reached. The composition of the mixed products varies within the following limits:

<table>
<thead>
<tr>
<th>Type I metal soap</th>
<th>40–10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type II metal soap</td>
<td>60–70</td>
</tr>
<tr>
<td>Organic compounds melting below 140°C</td>
<td>0–20</td>
</tr>
</tbody>
</table>

The metal components which can be employed in the present process in forming soaps I and II include the oxides, hydroxides, formates, or acetates of mono-, di- and tri-valent metals; for example, lead, zinc, magnesium, cadmium, calcium, baryum, strontium, aluminium, lithium, potassium, sodium, cerium, bismuth, manganese, tin, nickel and beryllium. The fatty acids which can be used are saturated, straight-chain fatty acids with from about 8 to about 24 carbon atoms. Instead of pure fatty acids, there can also be employed fatty acid mixtures as obtained by industrial processes. The latter contain varying amounts of unsaturated fatty acids like oleic acid, linolenic acid, linolenic acid or ricinoleic acid. As a rule, the amount of unsaturated fatty acids should not exceed 10 to 20% of the total amount of fatty acids. The unsaturated fatty acids normally form plastic soaps and therefore do not hinder the process. Larger quantities of unsaturated acids would only affect the milling properties of the final products, and are therefore undesirable.

The process of the invention is illustrated by the following examples.

**EXAMPLE 1**

Lead stearate, calcium stearate, 1:1
82.85 grams (g.) of stearic acid are heated to about 120°C and are admixed with 4.815 g. of calcium oxide, the latter being introduced in small portions. When the reaction is ended, 14.95 g. of lard is added to the resulting mixture, again in small portions. In order to accelerate the reaction, a few drops of water are sprayed into the melt. The reaction temperature can then be increased up to 150°C.

**EXAMPLE 2**

Barium-cadmium laurate: 37.5% barium laurate, 62.5% cadmium laurate
81.7 g. of lauric acid are heated to 130°C to 140°C and are admixed, while stirring, with 18.65 g. of cadmium hydroxide. The latter is added in small portions. When the reaction is completed, 14.55 g. of barium hydroxide monohydrate are stirred into the resulting reaction mixture. The product is then poured into a pan for cooling and can be ground thereafter without difficulty.

**EXAMPLE 3**

Barium-cadmium laurate: 30% barium laurate, 50% cadmium laurate, 20% lubricant
65.4 g. of lauric acid are heated together with 10 g. of a C₁₀–C₁₈ fatty alcohol and 10 g. of spermatic oil to 120°C to 130°C. The resulting mass is admixed while stirring with 14.92 g. of cadmium hydroxide. After completion of the reaction, 11.63 g. of barium hydroxide monohydrate are stirred in. If the melt becomes too viscous, the temperature can be increased to about 140°C to 150°C.

**EXAMPLE 4**

Barium-cadmium soap from hydrolysed coconut fatty acid: 51.6% barium soap, 28.4% cadmium soap, 20% lubricant
62.1 g. of hydrolysed coconut fatty acid are heated together with 20 g. of a C₁₀–C₁₈ fatty alcohol to about 120°C to 130°C, and 7.56 g. of cadmium hydroxide are stirred into the resulting mixture while stirring. After completion of the reaction, 16.55 g. of barium hydroxide are introduced. The reaction temperature can be raised to about 140°C to 150°C.

**What we claim is:**

1. A process for preparing a mixture of metal soaps consisting essentially of (a) from about 10 to about 40 percent by weight of at least one metal soap melting below about 140°C of a saturated, straight-chain fatty acid having from about 8 to about 24 carbon atoms per molecule and a metal selected from the group consisting of zinc, cadmium and magnesium, or a normal lead soap of said acid, and (b) from about 60 to about 70 percent by weight of at least one metal soap not melting below about 140°C of said acid and of a metal selected from the group consisting of lithium, potassium, sodium, barium, calcium, strontium, aluminium, cerium, bismuth, manganese, tin, nickel and beryllium, or a basic lead salt of said acid, which comprises reacting said acid with a metal compound selected from the group consisting of an oxide, a hydroxide and an acetate or formate, wherein the metal thereof is identified in (b) above, at a temperature above about 100°C in a melt of soap (g).

2. The process of claim 1, wherein reaction is effected at a temperature from about 100°C to about 150°C.

3. The process of claim 1, wherein reaction is effected in the presence of up to about 20 percent by weight of an organic additive selected from the group consisting of a wax, a long chain alcohol, a paraffin, a fatty acid ester, a fatty acid amide, a triglyceride and a phthalic acid ester melting between about 25°C and about 140°C.

4. A process for preparing a mixture of metal soaps consisting essentially of (a) from about 10 to about 40 percent by weight of at least one metal soap melting below about 140°C of a saturated, straight-chain fatty acid having from about 8 to about 24 carbon atoms per molecule and a metal selected from the group consisting of zinc, cadmium and magnesium, or a normal lead soap of said acid, and (b) from about 60 to about 70 percent by weight of at least one metal soap not melting below about 140°C of said acid and of a metal selected from the group consisting of lithium, potassium, sodium, barium, calcium, strontium, aluminium, cerium, bismuth, manganese, tin, nickel and beryllium, or a basic lead salt of said acid, which comprises reacting an excess of the molten fatty acid with a metal compound selected from the group consisting of an oxide, hydroxide and an acetate or formate, at least
one metal thereof being identified in (b) above and then after completion of the reaction convert the surplus of fatty acid with a metal compound selected from the group consisting of an oxide, hydroxide and an acetate or formate, at least one metal thereof being identified in (a) above.

5. The process of claim 1, wherein the mixture comprises approximately equal parts by weight of lead stearate and calcium stearate, formed by reacting about 3 molar proportions of stearic acid with 1 molar proportion of calcium oxide and then with about 0.6 molar proportion of litharge at a temperature from about 120° C. to about 150° C.

6. The process of claim 1, wherein the mixture comprises about 37.5 percent by weight of barium laurate and about 62.5 percent by weight of cadmium laurate, formed by reacting about 1.6 molar proportions of lauric acid with 1 molar proportion of cadmium hydroxide and then with about 0.3 molar proportion of barium hydroxide monohydrate at a temperature of about 140° C.

7. The process of claim 3, wherein the mixture comprises about 30 percent by weight of barium laurate, about 50 percent by weight of cadmium laurate and about 20 percent by weight of equal parts by weight of a C_{18}-C_{18} fatty alcohol mixture and of spermaceti, formed by reacting about 3 molar proportions of lauric acid with one molar proportion of cadmium hydroxide in the presence of said alcohol mixture and said spermaceti and then with about 0.6 molar proportion of barium hydroxide monohydrate at a temperature from about 120° C. to about 150° C.

8. The process of claim 3, wherein the mixture comprises about 52 percent by weight of barium soaps of coconut fatty acids, about 28 percent by weight of cadmium soaps of coconut fatty acids and about 20 percent by weight of a C_{18}-C_{18} fatty alcohol mixture, formed by reacting about 5.5 molar proportions of coconut fatty acids with one molar proportion of cadmium hydroxide in the presence of said alcohol mixture and then with about 1.7 molar proportions of barium hydroxide at a temperature from about 120° C. to about 150° C.

9. A mixture of metal soaps formed by the process of claim 1.

10. A mixture of metal soaps formed by the process of claim 3.

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U.S. Cl. X.R.

252—36, 39, 351, 407; 260—414
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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July 7, 1970

Alfred Szczepanek et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 14, "40° C." should read -- 140° C. --.
Column 2, line 72, cancel "component melting in the range of from about 250 C.".

Signed and sealed this 2nd day of March 1971.

(Seal)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

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Commissioner of Patents